Dioxins in ambient air and dry deposition in Korea

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Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans(PCDD/Fs), which are primarily originated from combustion process and distributed widely in environment. PCDD/Fs of gas and particle phase emitted into atmosphere from various sources go through various physical and chemical processes such as partition, decomposition, condensation, dispersion and deposition. Deposition process is an important because of removal of PCDD/Fs in atmosphere. The many studies have been carried out about PCDD/Fs in dry deposition and ambient air.[1~6] The objective of this study is to compare PCDD/Fs congener distributions containing ambient air and dry deposition. For this study, seasonal variations of PCDD/Fs concentrations were investigated.

Materials and methods

(1) Sampling

The dry deposition and ambient air samples were collected in spring, summer, fall and winter from April 2004 to January 2005 at one monitoring site located at Pohang, Korea. The dry deposition samples were collected for 24hour by using twenty British deposit gauge. The ambient air samples were collected according to the USEPA method by using high volume air sampler equipped with a quartz miro-fiber filter and poly urethane foam plugs(PUF). Each ambient air sample was collected at a flow of average 0.218m^3/min for 24hour. Before sampling, 2.4ng cleanup standard ($^{37}Cl_4$-2,3,7,8-TCDD) was spiked at polyurethane foam.

After sample collection, the dry deposition samples containing in polyethylene bottle were filtered by glass fiber filter and distilled water. The filtered samples were dried in a desiccator and then weighed. The filters of ambient air samples were weighed. All the samples were stored at under -20℃ until analyses.

(2) Extraction and Clean-up

All the samples were soxhlet extracted with 300mL toluene for above 18hour. The extracts were exchanged into hexane and then spiked with recovery standards. The clean-up procedure followed by multi-layer silica gel and alimina colume. The purified samples were spiked with internal standards($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$–1,2,3,7,8,9-HxCDD) and then concentrated to 100 $\mu\ell$ for HRGC/HRMS analyses.

(3) HRGC/HRMS analysis

All the samples were analyzed by high-resolution GC-mass spectrometry(SIM mode, resolution:10,000) with a HP6890 GC system(Hewlett- Packard, USA) coupled to an Autospec-ultima(Micromass, Manchester, UK) and a DB-5MS capillary column(60m x 0.32mm i.d.). The GC temperature program was 120 ^{o}C(held for 3 min), increased at 20 ^{o}C/min to 220 ^{o}C(held for 5 min), increased at 4 ^{o}C /min to 260 ^{o}C(held for 25 min). Injector temp. was 280 ^{o}C and injection was made on splitless mode(1 min). Helium at a pressure of 25 psi was used as carrier gas.

Results and Discussion

(1) The concentrations of PCDD/Fs

The seasonal average concentrations of PCDD/Fs containing in dry deposition and ambient air samples are summarized in Table 1. The dry deposition fluxes of 17 PCDD/Fs were 240.0, 58.4, 102.2 and 406.8 ng/m2/day in spring, summer, fall and winter. The average deposition flux of 12 samples for four seasons was 201.9 ng/m2/day. The total dry deposition flux was reported to increase with decreasing temperature, as particle

deposition dominated the dry deposition process and the more PCDD/Fs were adsorbed to particles at cooler temperature.[3]

The PCDD/Fs concentrations containing in particles in ambient air were 1.658, 1.254, 2.352 and 5.548 respectively. The seasonal pattern of PCDD/Fs concentrations in ambient air was similar to dry deposition. The seasonal order of PCDD/Fs concentration was winter, spring, fall and summer. The temperature of sampling period was as follows : spring 22.5 °C ; summer 28.9 °C ; fall 17.4 °C ; winter 4.8 °C.

Table 1 The seasonal average concentrations of PCDD/Fs containing in dry deposition and ambient air samples

	Dry deposition flux					Ambient air (Particle)				
	Spring	Summer	Fall	Winter	Ave.	Spring	Summer	Fall	Winter	Ave.
Concentration*	240.0	58.4	102.2	406.8	201.9	1.658	1.254	2.352	5.548	2.703
I-TEQ	3.1	1.5	2.6	3.7	2.7	0.082	0.052	0.071	0.119	0.081

* dry deposition flux unit : ng/m^2/day, ambient air unit : pg/m^3

(2) The contributions of 2,3,7,8-substituted PCDD/Fs congeners

The contributions of 2,3,7,8-substituted PCDD/Fs congeners containing in dry deposition and ambient air samples are summarized in Table 2. It is instructive to compare the pattern of PCDD/Fs in ambient air and deposition sampled concurrently at the same site because this yields information on the relative transfer efficiencies of the compounds.[3] The contribution patterns of PCDD/Fs congeners in dry deposition were similar

Table 2 The contributions of 2,3,7,8-substituted PCDD/Fs congeners containing in dry deposition and ambient air samples

Unit : %

2,3,7,8 congener		Dry deposition				Ambient air (Particle)			
		Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter
		n=3	n=3	n=3	n=3	n=3	n=3	n=3	n=3
PCDFs	2,3,7,8-TCDF	3.08	1.06	1.25	3.33	0.68	0.53	0.40	0.35
	1,2,3,7,8-PeCDF	3.77	1.93	1.67	2.96	1.69	0.67	0.82	0.11
	2,3,4,7,8-PeCDF	5.14	3.00	2.56	4.78	2.37	1.58	1.12	0.48
	1,2,3,4,7,8-HxCDF	5.31	4.29	3.84	5.05	4.06	3.98	3.63	2.81
	1,2,3,6,7,8-HxCDF	4.62	3.76	2.90	4.19	4.85	4.62	3.22	2.33
	2,3,4,6,7,8-HxCDF	8.22	5.09	4.03	6.41	6.57	4.69	3.24	2.14
	1,2,3,7,8,9-HxCDF	2.74	1.58	1.40	2.47	2.51	0.92	1.01	0.34
	1,2,3,4,6,7,8-HpCDF	17.13	15.15	13.03	16.02	17.96	22.62	55.10	69.30
	1,2,3,4,7,8,9-HpCDF	3.43	2.70	2.70	3.70	3.63	4.56	0.59	0.32
	OCDF	17.13	15.56	17.21	12.33	14.01	15.57	7.41	10.39
PCDDs	2,3,7,8-TCDD	0.46	0.27	0.31	0.46	0.21	0.35	0.12	0.05
	1,2,3,7,8-PeCDD	1.23	0.93	1.08	1.58	1.47	1.21	0.33	0.25
	1,2,3,4,7,8-HxCDD	0.34	0.49	0.10	0.49	2.97	3.39	0.88	0.68
	1,2,3,6,7,8-HxCDD	1.54	1.74	2.16	1.60	1.04	0.72	1.27	0.72
	1,2,3,7,8,9-HxCDD	0.17	0.76	0.27	0.12	1.30	0.73	1.09	0.30
	1,2,3,4,6,7,8-HpCDD	8.56	11.38	13.52	9.86	10.52	8.80	7.57	3.91
	OCDD	17.13	30.30	31.96	24.65	24.17	25.08	12.18	5.53
	PCDFs	70.56	54.12	50.60	61.24	58.33	59.73	76.54	88.56
	PCDDs	29.44	45.88	49.40	38.76	41.67	40.27	23.46	11.44

to ambient air. However, the contributions of low chlorinated compounds of PCDF in dry deposition were higher than ambient and high chlorinated compounds of PCDF showed opposed result.

(3) Dry deposition velocities

One method that can be used to determine the efficiency of the removal of particle-phase PCDD/Fs from the atmosphere is the calculation of the dry depositionvelocity.[7] The dry deposition velocities of PCDD/Fs were summarized in Table 3. The dry deposition velocity of spring and winter was 0.23 and 0.49cm/s, respectively. However, the dry deposition velocity of summer and fall showed very low value, which is 0.07 and 0.09cm/s, respectively. These values expose large difference compared with deposition measurement by Koester and Hites.[8]

Table 3 The dry deposition velocities of PCDD/Fs

Congener	Spring	Summer	Fall	Winter
2,3,7,8-TCDF	0.76	0.11	0.16	0.81
1,2,3,7,8-PeCDF	0.37	0.15	0.10	2.32
2,3,4,7,8-PeCDF	0.36	0.10	0.12	0.85
1,2,3,4,7,8-HxCDF	0.22	0.06	0.05	0.15
1,2,3,6,7,8-HxCDF	0.16	0.04	0.05	0.15
2,3,4,6,7,8-HxCDF	0.21	0.06	0.06	0.25
1,2,3,7,8,9-HxCDF	0.18	0.09	0.07	0.63
1,2,3,4,6,7,8-HpCDF	0.16	0.04	0.01	0.02
1,2,3,4,7,8,9-HpCDF	0.16	0.03	0.23	0.99
OCDF	0.20	0.05	0.12	0.10
2,3,7,8-TCDD	0.37	0.04	0.13	0.72
1,2,3,7,8-PeCDD	0.14	0.04	0.16	0.54
1,2,3,4,7,8-HxCDD	0.02	0.01	0.01	0.06
1,2,3,6,7,8-HxCDD	0.25	0.13	0.09	0.19
1,2,3,7,8,9-HxCDD	0.02	0.06	0.01	0.03
1,2,3,4,6,7,8-HpCDD	0.14	0.07	0.09	0.21
OCDD	0.12	0.07	0.13	0.38
Mean	0.23	0.07	0.09	0.49

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